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Compressive Pressure, Spatial Confinement of Ions, and Adiabatic Heat Generation in Binary Strong Electrolyte Solutions by an External Electric Field

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Abstract

In this paper, we make use of the exact hydrodynamic solution for the Stokes equation for the velocity of a binary ionic solution that we have recently obtained, and show that the nonequilibrium pressure in an electrolyte solution subjected to an external electric field can be not only compressive, but also divergent in the region containing the coordinate origin at which the center ion of its ion atmosphere is located. This divergent compressive pressure implies that it would be theoretically possible to locally confine the ion and also to adiabatically generate heat in the local by means of the external electric field. The field dependence of pressure and thus heat emission is numerically shown and tabulated together with the theoretical estimate of its upper bound, which is exponential with respect to the field strength. It shows that, theoretically, the Coulomb barrier between nuclei in the electrolyte solution (e.g., the ion and a nucleus of the solvent molecule) can be overcome so as to make them fuse together, if no other effects intervene to prevent it.

I. Introduction

In a previous work¹ on the solution of the Navier–Stokes (NS) equation—in fact, the Stokes equation—for flow in electrolyte solutions subjected to an external electric field, we have obtained exact solutions for the flow velocity of the medium and the local nonequilibrium pressure as functions of the applied field strength and other characteristic parameters of the system. The solutions show that both the velocity of the countercurrent to the movement of ions pulled by the applied external electric field and the (nonequilibrium) pressure are divergent at the coordinate origin at which the center of the ion atmosphere of an ion is positioned, whereas outside the region the pressure profile is finite and can be positive. In particular, the excess nonequilibrium pressure on the center ion not only is nonuniform in space, but also becomes negative and divergent as the center ion is approached. This means that the pressure on the center ion is compressive. Moreover, as will be shown, the nonequilibrium part of the pressure is exponentially increasing in magnitude with respect to the field strength as the field strength increases.

The divergent behavior of nonequilibrium pressure thus suggests, first of all, that the compressional effect of the field gives rise to an emission of heat (thermodynamic in origin), apart from the usual Ohmic heat due to resistance. Thus, for example, it may explain the extraordinary heat generation which was observed by Eckstrom and Schmeltzer during their conductance experiments² many years ago. Secondly, the spatially nonuniform and divergent compressive pressure suggests a possibility of spatially confining the ion with the external electric field together with the concerted help of equally divergent countercurrent to the ions pulled by the field, while the ions on the periphery of the ion atmosphere are delocalized and conduct currents. This latter behavior was shown by the velocity profiles^{3,4} calculated from the solution of the Stokes equation

show similarly divergent profiles. This possibility of locally confining ions by means of an external electric field seems quite interesting and potentially rather significant. For example, at least theoretically, the spatially confined ions can overcome the Coulomb barrier of nuclei if a sufficiently high field is applied, and it would then be probable that they might fuse together. In this paper, we would like to examine more closely the compressive pressure with respect to the spatial position and also its behavior with respect to the applied field strength.

We consider a binary strong electrolyte solution subjected to an external electric field applied in the positive x direction in the cylindrical coordinate system fixed on a center ion of its ion atmosphere. Since the field is axially symmetric around the x axis, cylindrical coordinates are natural coordinates to choose; see Fig. 1. Let the radial coordinate and azimuthal angle in the plane perpendicular to the field axis be denoted ρ and θ , respectively. Because of the axial symmetry of the field, the solution of the NS equation⁵ then is independent of angle θ and hence is a function of x and ρ only.

In the Onsager theory of electrolyte conductance⁶ the local field in the ionic solution subjected to the external field can be calculated from the Onsager–Fuoss (OF) equations⁷ and the Poisson equation,⁸ which are coupled to each other. The so-obtained local field is then used in the NS equation (Stokes equation in fact) for the calculation of velocity of the medium in the external field, and it provides the spatial profiles of the countercurrent to the ionic migration in the electrolyte solution under the influence of the external electric field, as shown in the previous paper^{1,4} of this series. Consistently with the velocity, the local nonequilibrium excess pressure is simultaneously obtained from the NS equation. The formal Fourier transform solutions for velocity and pressure have been explicitly calculated as functions of position variables in a previous paper.^{1,4} An application of the result for the velocity to study the equivalent conductance of

binary electrolyte solutions³ is in progress, especially, with regard to the Wien effect^{9,10,12}—a nonlinear (non-Coulombic) field dependence of conductance.

II. Local Nonequilibrium Pressure

The local nonequilibrium pressure is given in the cylindrical coordinates (r, ρ, θ) by the formula^{1,4}

$$\Delta p = p - p_0 = \frac{zeX\kappa^2}{4\pi^2} \Delta \hat{p}(r, \rho), \quad (1)$$

where p is the pressure, p_0 is the equilibrium (hydrostatic) pressure, $\Delta \hat{p}$ is the reduced excess nonequilibrium pressure, which is independent of angle θ because of the cylindrical symmetry of the system. Other symbols are: z is the absolute value of the charge number of the binary electrolyte, e is the electric charge, κ is the inverse Debye length (Debye parameter)

$$\kappa = \sqrt{\frac{4\pi e^2 n}{Dk_B T} \sum_k z_k^2 c_k} \quad \left(c_k = \frac{n_k}{n}; \text{ mole fraction of } k \right) \quad (2)$$

with k_B denoting the Boltzmann constant, T the absolute temperature, n the density, and D the dielectric constant, and finally the excess reduced nonequilibrium pressure is given by the formula

$$\begin{aligned} \Delta \hat{p}(\bar{x}, r) = & -\frac{\pi \bar{x}}{2(\bar{x}^2 + r^2)^{3/2}} \\ & - \frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-\bar{x}y} y (1 + \sqrt{2}\xi y + \sqrt{1 + 2\xi^2 y^2})}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 r) \\ & + \frac{\pi}{2} \int_0^1 dy \frac{e^{-\bar{x}y} \sqrt{2}\xi y^2 (1 - \sqrt{2}\xi y)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_3 r). \end{aligned} \quad (3)$$

In this expression, the axial coordinate \bar{x} and the radial coordinate r are reduced distances scaled by $\sqrt{2}\kappa^{-1}$

$$\xi = \frac{zeX}{k_B T \kappa}, \quad \bar{x} = \kappa x / \sqrt{2}, \quad r = \kappa \rho / \sqrt{2}, \quad (4)$$

$$\bar{\omega}_1 = \sqrt{1 - y^2 + \sqrt{1 + 2\xi^2 y^2}}, \quad \bar{\omega}_3 = \sqrt{1 - y^2}, \quad (5)$$

and $I_0(s)$ is the zeroth order regular Bessel function^{13,14} of second kind of argument s ; it tends to unity as $s \rightarrow 0$, but grow exponentially as $s \rightarrow \infty$. Therefore as the reduced field strength ξ increases, $I_0(\bar{\omega}_i r)$ increases exponentially with respect to ξ . Henceforth for the sake of notational brevity the overbar in the reduced variable \bar{x} will be omitted and by x the reduced distance defined in Eq. (4) will be understood.

Therefore in some regions of (x, r) the integrals grow exponentially with respect to ξ as will be graphically demonstrated later. It is also easy to show that the estimates of the integrals indeed grow exponentially with respect to ξ :

$$\overline{\langle \Delta p \rangle} \leq \frac{e^{\sqrt{2(1+\xi^2)}R}}{\sqrt{2\pi}R^{3/2}} E(\xi), \quad (6)$$

where

$$E(\xi) = \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{(1 + \sqrt{2}\xi y + \sqrt{1 + 2\xi^2 y^2})}{(1 + 2\xi^2 y^2) (1 - y^2 + \sqrt{1 + 2\xi^2 y^2})^{1/4}}. \quad (7)$$

The integrals in Eq. (3) are easily computed numerically, and $\Delta\hat{p}$ shows a negative region in the neighborhood of the coordinate origin for all values of ξ , becoming negative infinite as the origin is approached, as will be shown in Fig. 2 below.

Since ions are spherical and their force fields are spherically symmetric, for the investigation in mind it is convenient to cast the pressure in spherical coordinates. The cylindrical coordinates are related to the spherical coordinates by the relations

$$\begin{aligned} \theta &= \varphi, \\ x &= R \cos \vartheta, \\ r &= R \sin \vartheta, \end{aligned} \quad (8)$$

where R , ϑ , and φ are the radial, polar, and azimuthal angle coordinates (in reduced units) in the spherical coordinate system. Owing to $\Delta\hat{p}$ being scalar, the

spherical coordinate representation of $\Delta\hat{p}(R, \vartheta)$ is simply given by the formula

$$\begin{aligned}\Delta\hat{p}(R, \vartheta) = & -\frac{\pi \cos \vartheta}{2R^2} \\ & -\frac{\pi}{4} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{e^{-yR \cos \vartheta} y \left(1 + \sqrt{2}\xi y + \sqrt{1 + 2\xi^2 y^2}\right)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_1 R \sin \vartheta) \\ & +\frac{\pi}{2} \int_0^1 dy \frac{e^{-yR \cos \vartheta} \sqrt{2}\xi y^2 (1 - \sqrt{2}\xi y)}{1 + 2\xi^2 y^2} I_0(\bar{\omega}_3 R \sin \vartheta). \quad (9)\end{aligned}$$

The behavior of this excess nonequilibrium pressure is shown in Fig. 2. This pressure is divergent in the region in the immediate neighborhood of the origin, but outside the region, it has also a positive region, and it means that the ion in the neighborhood of the origin is compressed by the divergent force toward the center by the medium under the influence of the external electric field. We would like to examine a quantitative measure of such compression and its relation to heat. In this connection, we remark that a large heat emission was observed by Eckstrom and Schmeltzer² during their conductance experiment on electrolyte solutions.

We now calculate the excess nonequilibrium pressure on the unit area of the surface of a sphere of radius R . The first term on the right of Eq. (9) vanishes on integration of the surface. It should be also noted that the integrals are not uniformly convergent to a finite value in the entire region of R . So, the parameter R should not be taken equal to zero within the integrals before fully evaluating them. Therefore we find

$$\begin{aligned}\langle \Delta p \rangle = & -\frac{zeX\kappa^2}{8\pi} \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{y \left(1 + \sqrt{2}\xi y + \sqrt{1 + 2\xi^2 y^2}\right)}{1 + 2\xi^2 y^2} \times \\ & \int_0^\pi d\vartheta \sin \vartheta e^{-yR \cos \vartheta} I_0(\bar{\omega}_1 R \sin \vartheta) \\ & +\frac{zeX\kappa^2}{4\pi} \int_0^1 dy \frac{\sqrt{2}\xi y^2 (1 - \sqrt{2}\xi y)}{1 + 2\xi^2 y^2} \times \\ & \int_0^\pi d\vartheta \sin \vartheta e^{-yR \cos \vartheta} I_0(\bar{\omega}_3 R \sin \vartheta). \quad (10)\end{aligned}$$

The two-dimensional quadratures are fairly easy to compute numerically. The results of computation are presented in Fig. 3, in which we have plotted a reduced $\langle \Delta p \rangle$ vs. $\log \xi$:

$$\begin{aligned}
\Psi/\xi &= -\frac{\langle \Delta p \rangle}{8\pi k_B T \kappa^3 \xi} \\
&= \int_0^{\sqrt{2(1+\xi^2)}} dy \frac{y \left(1 + \sqrt{2\xi} y + \sqrt{1 + 2\xi^2 y^2} \right)}{1 + 2\xi^2 y^2} \times \\
&\quad \int_0^\pi d\vartheta \sin \vartheta e^{-yR \cos \vartheta} I_0(\varpi_1 R \sin \vartheta) \\
&\quad - \int_0^1 dy \frac{2\sqrt{2\xi} y^2 (1 - \sqrt{2\xi} y)}{1 + 2\xi^2 y^2} \times \\
&\quad \int_0^\pi d\vartheta \sin \vartheta e^{-yR \cos \vartheta} I_0(\varpi_3 R \sin \vartheta). \tag{11}
\end{aligned}$$

Note that here Ψ is defined by

$$\Psi = -\frac{\langle \Delta p \rangle}{8\pi k_B T \kappa^3}. \tag{12}$$

Since $\langle \Delta p \rangle$ is the force exerted on unit area of the surface of radius R , in fact Ψ is a reduced work relative to $k_B T$ to compress the fluid to volume κ^{-3} of a sphere by the external field in which the ion is confined. As is evident from Fig. 2, $\langle \Delta p \rangle$ is negative, and it can be deduced from Fig. 3 that $\langle \Delta p \rangle$ tends to $\exp(c\xi)$ ($c > 0$) as the field strength increases in confirmation of the theoretical estimate given in Eq. (6). Since the bound of Ψ is deduced from Eq. (6)

$$|\Psi| \leq \frac{E(\xi)}{\sqrt{2\pi} R^{3/2}} \exp \left[R \sqrt{2(1+\xi^2)} \right] \tag{13}$$

and it can be deduced numerically that

$$\lim_{\xi \rightarrow \infty} \xi E(\xi) = \text{finite but not zero.}$$

The parameters $R = 0.001$, etc. chosen for the plot in Fig. 3 are the reduced radii of the confining space. This plot shows that $\langle \Delta p \rangle$ gets more and more compressive as the value of R decreases. Note that $\xi = zeX/k_B T \kappa$ and

reduced distance R is defined by $R = \kappa \hat{R} / \sqrt{2}$, where \hat{R} is the radial coordinate in the spherical coordinate system in actual units. We also present Table 1 for the Ψ/ξ values used for Fig. 3 in the high end regime of ξ . We remark that for electrolyte solutions of concentration on the order of 10^{-3} mole/liter at normal temperature, the Debye radius κ^{-1} is on the order of 30 Å.

By using $\langle \Delta p \rangle$, it is possible to estimate the molar heat emission in the electrolyte solution in an adiabatic condition (constant entropy S) that accompanies the applied field:

$$(\Delta h)_S = \bar{v} \langle \Delta p \rangle_S, \quad (14)$$

where \bar{v} is the molar volume of the solution. Because $\langle \Delta p \rangle < 0$ in general, a heat is generated by the compression effect of the field, and it appears to explain the phenomenon of excessive heat generation observed by Eckstrom and Schmeltzer² during their conductance experiment. This heat is obviously different from the heat for the Coulomb heating effect, but a nonequilibrium thermodynamic effect, which is probably the underlying cause for the claim of cold fusion.

III. Discussion and Concluding Remarks

The NS equation for velocity of the medium in binary electrolyte solutions subjected to an external electric field can be exactly solved by using the local potentials provided by the solutions of the coupled differential equations of Onsager–Fuoss equations⁷ for ionic pair distribution functions and the Poisson equations⁸ for potentials according to the Onsager–Wilson theory of electrolyte conductance.¹⁰ In the present article, on the basis of the solution of the NS equation presented in a previous article¹ we have made a deduction on the possibility of local confinement of ions by means of an electric field on the basis of the solution of the NS equation for binary electrolyte solutions. More

specifically, the nonequilibrium pressure obtained from the NS solution can be shown to be compressive and thus emissive of heat, and this compressive force presents a theoretical possibility of locally confining ions to a small space by an external electric field. This compressive force is asymptotically proportional to a product of field times an exponential function of the field as shown in Fig. 2. This local confinement effect is an outcome of collective motion of ions and their ion atmosphere and their mutual interactions with each other and with the external electric field, producing a countercurrent (velocity) to the ionic motions in the field which is nonuniformly distributed in space. It is not clear to what extent of field strength the present theory is applicable to electrolyte solutions before other complicating processes may set in. Only experiment can explore the range.

It should be noted that the velocity of the countercurrent is nonuniformly distributed in space, being singular in a region and finite in another, especially in the periphery of ion atmosphere and thus producing a finite electrophoretic effect. Thus in this latter region the ions are mobile and produce conduction.³ Thus the fact that some ions are locally confined does not contradict that the electrolyte solutions under the influence of the external electric field conduct electrical currents.

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Figure Captions

Fig. 1. The coordinate system.

Fig. 2. The reduced excess nonequilibrium pressure cut at reduced radius $R = 0.001$ in spherical coordinates for the field strength $\xi = 1$. At this field strength $\Delta p \equiv \Delta \hat{p}(R, \vartheta)$ is negative except for two regions of ϑ and the range of $R \gtrsim 1$. Δp gets more and more negative as ξ increases.

Fig. 3. Reduced force on the surface of the sphere of radius R as a function of ξ for a few cases of R . The reduced force Ψ is defined by $\Psi = -\langle \Delta p \rangle / 8\pi k_B T \kappa^3$. The reduced force rises exponentially as ξ increases.

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Figure 1:

Table1

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Figure 2:

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Figure 3:

Table 1: Negative reduced pressure vs ξ

$R = 0.1$		$R = 0.01$		$R = 0.001$	
ξ	Ψ/ξ	ξ	Ψ/ξ	ξ	Ψ/ξ
1	4.6732	1	4.6707	1	4.6707
4	1.2094	30	0.1656	400	0.01256
7	0.7099	60	0.08416	800	0.00642
10	0.5112	90	0.05738	1200	0.004448
13	0.4092	120	0.04440	1600	0.003533
16	0.3490	150	0.03703	2000	0.003062
19	0.3119	180	0.03255	2400	0.002838
22	0.2901	210	0.02984	2800	0.00279
25	0.2792	240	0.02836	3200	0.002899
28	0.2776	270	0.02785	3600	0.003176
31	0.2846	300	0.02823	4000	0.00366
34	0.3006	330	0.02950	4400	0.004421
37	0.3269	360	0.03175	4800	0.005569
40	0.3654	390	0.03516	5200	0.007278
43	0.4194	420	0.03100	5600	0.009811
46	0.4932	450	0.04665	6000	0.01358
49	0.5938	480	0.05569	6400	0.01920
52	0.7281	510	0.06785	6800	0.02763

Table 2: Negative reduced pressure vs ξ

$R = 0.1$		$R = 0.01$		$R = 0.001$	
ξ	Ψ/ξ	ξ	Ψ/ξ	ξ	Ψ/ξ
55	0.9085	540	0.08419	7200	0.04036
58	1.1510	570	0.1062	7600	0.05971
61	1.4776	600	0.1357	8000	0.08929
64	1.9221	630	0.1757	8400	0.1348
67	2.5212	660	0.2298	8800	0.2050
70	3.3360	690	0.3033	9200	0.3142
73	4.4480	720	0.4036	9600	0.4845
76	5.9707	750	0.5409	10000	0.7516
79	8.0773	780	0.7293	10400	1.1720
82	10.966	810	0.9889	10800	1.8363
85	14.961	840	1.3476	11200	2.8901
88	20.501	870	1.8446	11600	4.5672
91	28.257	900	2.5358	12000	7.2451
94	39.02	930	3.4987	12400	11.5336
97	54.067	960	4.8451	12800	18.4213
100	75.155	990	6.7313	13200	29.5126

Table 1 (continued)

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